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and Space Administration

Scientific and Technical
Information Branch

Summary

The sliding friction behavior of the semiconductors silicon, and gallium arsenide in contact with pure metals was studied. Friction experiments were conducted at room temperature (20 to 30 °C) in room air and in a vacuum of 10^{-9} torr (10^{-7} N/m²). Five transition metals, titanium, tantalum, nickel, palladium, and platinum, slid on a single-crystal silicon (111) surface in the [11 $\bar{2}$] crystallographic direction. Four metals, indium, nickel, copper, and silver, slid on a single-crystal gallium arsenide (100) surface in the [011] direction. The sliding velocities were 1.4 mm/s in room air and 0.2 mm/s in vacuum. The loads were 10 to 100 g in room air and 10 g in vacuum.

The friction of semiconductors in contact with metals depended on a Schottky barrier height formed at the metal-semiconductor interface. Metals with a higher barrier height on semiconductors gave lower friction. From titanium (barrier height $\phi_b = 0.50$ eV) to platinum ($\phi_b = 0.81$ eV) sliding on silicon, the coefficient of friction decreased linearly with increasing barrier height. The effect of the barrier height on friction behavior for argon-sputtered surfaces in vacuum was more specific than that for the surfaces containing surface films in room air. Similar effects were found for gallium arsenide in contact with metals. With the silicon surface sliding on titanium, many silicon particles back-transferred. In contrast a large quantity of indium transferred to the gallium arsenide surface for gallium arsenide sliding on indium in vacuum.

Introduction

Physical and chemical properties of contacting materials play an important role in the tribological phenomena of solids as well as their mechanical characteristics. A considerable number of studies have been conducted for metal-metal contacts. Melting point and crystal structure of metals affect adhesive behavior (ref. 1). Friction and wear of metals are closely related to mutual solubility of two mating metals (refs. 2 to 4). Only a few tribological experiments for metal-semiconductor contacts, however, have been conducted. Although surface fracture, friction, and wear were studied for

silicon and germanium in contact with metals (refs. 5 to 8), the effects of the physical properties of the metal-semiconductor interface on tribological behavior have not been addressed.

In a recent study examining the surface change occurring during sliding contact for metals, semiconductor materials formed on the sliding surface (ref. 9). When the semiconductor formed on the metal surface, it changed the wear phenomenon and decreased the wear of metals. This result indicates that the semiconductor is an important material to be considered for tribological problems. This report presents a study of the tribological behavior of two semiconductors in sliding contact with metals.

When a semiconductor comes into contact with a metal, the surface state is remarkably different from the metal-metal interface. A barrier is formed by a bending of the electron band near the semiconductor surface, and the barrier height is one of the most important factors in the characterization of the metal-semiconductor interface. Although in the first model proposed by Schottky (ref. 10) and Mott (ref. 11) the barrier height depended on the metal work and the electron affinity of semiconductors, experimental results did not coincide with this model. For this discrepancy Bardeen (ref. 12) put forward another explanation for semiconductor surface state. According to his concept, the barrier height is restricted by the presence of an insulating surface film and is almost independent of the contacting metal. However, subsequent experiments measuring the precise barrier height at the metal-semiconductor interface revealed that the barrier height depended on the metal, although the correlation was weaker than predicted in the Schottky-Mott model (refs. 13 to 18 and data from Ph.D. thesis by B. L. Smith, Manchester University, 1969). The barrier height was related to chemical and physical properties of both metal and semiconductor. The relations of the barrier height to many factors, such as the heat of formation of metal silicides (ref. 19), the eutectic temperature of transition metal silicides (ref. 20), and the chemical bonding of the metal-silicon interface (ref. 21), have been recently discussed for silicon in contact with the transition metals.

An interesting relation between barrier height and the chemical affinity of the transition metals to silicon has been reported by Andrews and Phillips (ref. 19). They

found a simple linear correlation of the barrier height of the system transition-metal silicide and silicon with the formation energy of the metal silicide. This characteristic of the metal-silicon interface is closely related to the formation of an intimate contact at the interface. The contribution of barrier height to the formation of intimate contact at the metal-semiconductor interface is assumed to give a similar correlation between barrier height and friction behavior of semiconductors in contact with metals.

This investigation determined the effect of barrier height at the metal-semiconductor interface on the tribological behavior of the semiconductor. In a recent experiment examining the doping effect for silicon, friction behavior was sensitive to the P- or N-type electron state of silicon in contact with gold metal (ref. 6). In this study the friction behavior of silicon and gallium arsenide in sliding contact with pure metals in high vacuum and in room air were determined. The friction behavior for each semiconductor is discussed with reference to the properties of the metal-semiconductor interface.

Materials

The semiconductors used in these experiments were silicon and gallium arsenide. Silicon was a single-crystal plate of (111) orientation. Gallium arsenide was an undoped single-crystal plate of (100) orientation. Both of the specimens were polished, and the roughness R_{max} was less than $0.01 \mu\text{m}$.

The metals used as pin specimens were pure polycrystalline titanium, tantalum, nickel, palladium, platinum, indium, copper, and silver. Barrier heights of the metals on silicon and/or gallium arsenide (refs. 12 to 17 and data from Ph.D. thesis by B. L. Smith, Manchester, University, 1969) are summarized in table I.

Five metals, Ti, Ta, Ni, Pd, and Pt, slid on the silicon (111) surface parallel to the [112] crystallographic direction. Four metals, In, Ni, Cu, and Ag, slid on the gallium arsenide (100) surface parallel to the [011] direction. The diameter of each pin specimen was 3.18 mm, and the sliding surface was hemispherical. Sliding surfaces were polished with $0.3\text{-}\mu\text{m}$ aluminum powder. Both pin and plate specimens were cleaned with ethyl alcohol in an ultrasonic cleaner before each experiment.

Apparatus

Two different apparatuses were used in this investigation. Both apparatuses were pin and plate type devices. The device used for the experiments in room air is shown in figure 1. The pin specimen was mounted on a gimbal. Friction force was measured by strain gages mounted on a flat of the beam that was positioned near the pin specimen. Data were reproducible within 5 percent. Load was applied to the pin specimen with weights of 10 to 100 g (0.1 to 1.0 N).

The semiconductor specimen was mounted on a 25.4-mm cubic block. The block was then mounted on a stage which moved in reciprocating motion with a 10-mm stroke. The moving speed was 1.4 mm/s in both directions. In each experiment the pin specimen slid on the same 10-mm path of the semiconductor surface 30 times in each direction. The experiments were conducted in room air and at room temperature (21 to 23 °C, 30- to 35-percent relative humidity).

The apparatus used for the experiments in vacuum was enclosed in a vacuum system. The device for measuring load and friction is shown in figure 2. A gimbal-mounted beam projected into the vacuum system. The beam had two flats, normal to each other, for the mounting of strain gages. The end of the beam contained the metal pin specimen. The semiconductor specimen was mounted on

TABLE I.—BARRIER HEIGHTS OF METALS ON SI AND/OR GaAs

Metal	Purity, percent	Barrier height of Si, eV		Barrier height of GaAs, eV	
		Chemically etched	Cleaved	Chemically etched	Cleaved
Titanium	99.97	^a 0.50	Not measured	—	—
Tantalum	99.996	^b 0.58	Not measured	—	—
Nickel	99.995	^c 0.66	^d 0.69	^e 0.80	Not measured
Palladium	99.99	^c 0.72	^d 0.81	—	—
Platinum	99.99	^c 0.81	^d 0.85	—	—
Indium	99.999	—	—	^f 0.64	^g 0.75
Copper	99.999	—	—	^f 0.85	^g 0.85
Silver	99.999	—	—	^e 0.92	^g 0.92

^aRef. 12.

^bRef. 16.

^cRef. 13.

^dRef. 17.

^eRef. 14.

^fData from Ph.D. thesis by B. L. Smith, Manchester University, 1969.

^gRef. 15.

a cubic block. The block, made of ceramic (thermal and electrical insulator), was mounted to a manipulator beam. The surface of the block to which the semiconductor specimen was mounted was coated with a hafnium-sputtered film in order to achieve sputtering and heating of the semiconductor specimens. A Chromel-Alumel thermocouple buried just under the semiconductor specimen measured the temperature during specimen heating. Load was applied by

manipulating the block toward the pin and was measured by a strain gage. The load applied was 10 g (0.1 N). Frictional force was measured by the strain gage normal to that used to measure load. The error in measurement was 5 percent. The pin specimen slid in a single path of a 12-mm stroke on the semiconductor surface. Sliding velocity was 0.2 mm/s. The vacuum system was a conventional vacsorb ion-pumped system capable of achieving a pressure of 10^{-9} torr (10^{-7} N/m²) as measured by a nude ionization gage. The experiments were conducted at room temperature (21 to 23 °C) at a pressure of 10^{-9} torr.

Experimental Procedure for the Vacuum System

After the specimens were placed in the vacuum chamber, the system was evacuated. The system was baked out overnight at 260 °C (150 °C for the indium pin), after which the pressure was in the 10^{-7} N/m² range. Argon gas was bled into the vacuum system to a pressure of 10^{-1} N/m². A 1000-V direct-current potential was applied to the specimen, and it was sputter bombarded for a period of 30 min. Since Si and GaAs are semiconductors, when they were sputtered, a direct-current potential was applied to a hafnium-sputtered film on the ceramic block to achieve sputtering of the specimens.

Since the argon sputter bombardment of the GaAs produced changes in the initial surface composition (refs. 22 to 24), the method of cleaning GaAs was different from that for Si and metals. A sputtering and annealing

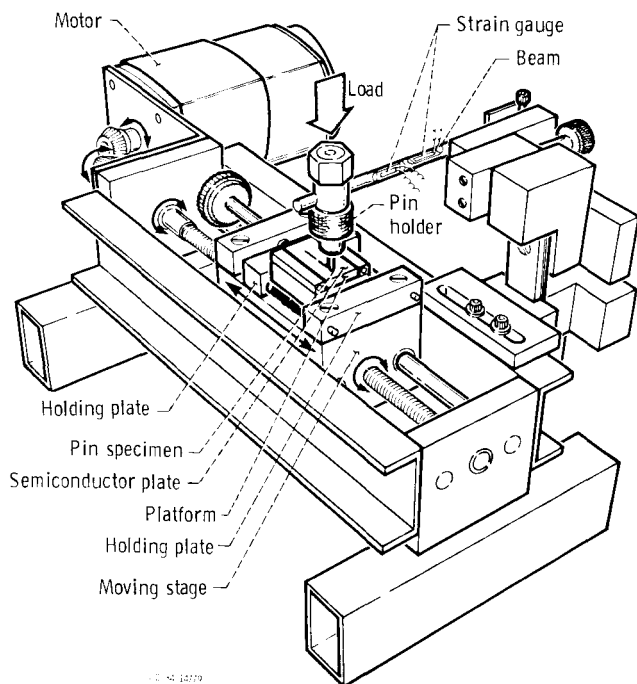


Figure 1.—Friction apparatus in room air.

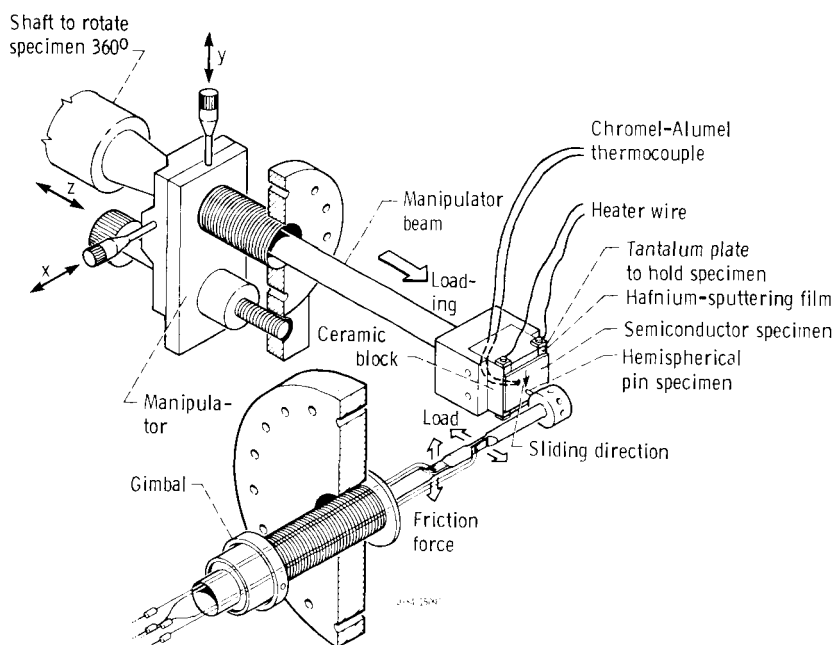


Figure 2.—Friction apparatus in vacuum system.

method was used in the experiment with GaAs (refs. 23 and 24).

After argon gas was bled into the system to a pressure of 10^{-1} N/m², a 300-V direct-current potential was applied for a period of 30 min. The system was evacuated again to a pressure of 10^{-6} to 10^{-7} N/m². The GaAs was annealed at 520 to 550 °C for a period of 60 min. The GaAs specimen was heated indirectly by a resistance heating of the hafnium film coated on the ceramic block. All friction experiments were conducted with the system reevacuated to a pressure of 10^{-7} N/m² (10^{-9} torr).

Results and Discussion

Friction With Silicon

Silicon is a highly polarizable semiconductor, and it is very active when in contact with transition metals (refs. 19 and 21). The friction behavior for silicon with these metals was examined in this study. Coefficients of friction as a function of load for five transition metals, titanium, tantalum, nickel, palladium, and platinum, slid on the silicon (111) surface in room air are presented in figure 3. The coefficient of friction in vacuum (10^{-9} torr) for all five metals sliding on silicon is summarized in table II. Stick-slip motion was found for all the metals slid on silicon. This behavior was similar to that previously reported (ref. 8). An example of the stick-slip motion is exhibited in figure 4. The coefficients of friction

TABLE II.—COEFFICIENT OF FRICTION FOR METALS SLID ON SILICON IN VACUUM AND ROOM AIR

[Load, 10 g.]

Metal	Coefficient of friction	
	In vacuum (10^{-9} torr)	In room air
Titanium	7.3	0.73
Tantalum	6.7	.68
Nickel	5.2	.60
Palladium	4.0	.41
Platinum	3.2	.30

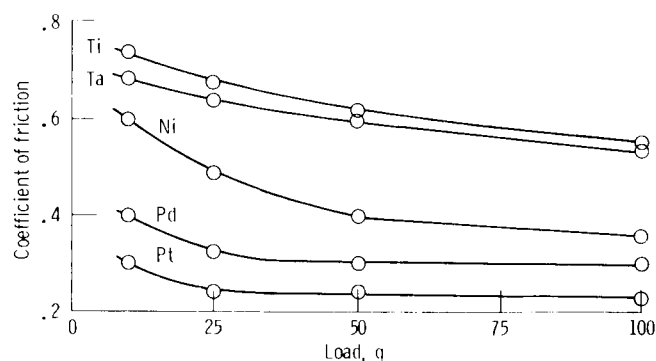


Figure 3.—Coefficient of friction as function of load for metals slid on silicon (111) surface in room air. Sliding velocity, 1.4 mm/s.

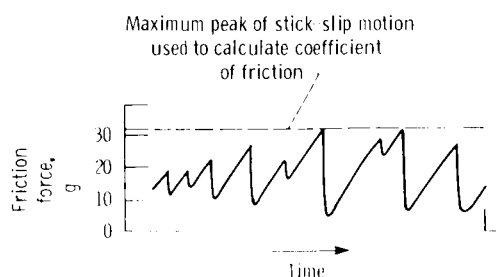


Figure 4. Stick-slip motion for silicon in sliding contact with platinum in vacuum (10^{-9} torr). Load, 10 g; sliding velocity, 0.2 mm/s.

presented in figure 3 and table II are the maximum peak values measured in the stick-slip motion for each sliding pass indicated in figure 4. In room air the friction behavior was very sensitive to the presence of surface films, as previously reported (ref. 8). In the first stage of sliding friction was much lower (coefficient of friction $\mu=0.2$ to 0.3). However, friction gradually increased with repeated sliding and achieved a steady-state value after 6 to 10 passes of sliding on the same path. The coefficients of friction plotted in figure 3 are the values measured after the steady state was achieved. The results of figure 3 and table II indicate that the coefficient of friction for silicon in contact with metals depended on the mating metals. Titanium presented the highest friction among the fine metals. With tantalum, nickel, and palladium, coefficients of friction were lower. Platinum presented the lowest friction. The influence of metals on the frictional behavior did not change when the load varied from 10 to 100 g. The effects of load on the coefficient of friction for each metal were the same. The coefficient of friction was higher when a lower load was applied. The change in coefficient of friction with a change in metal was greater in vacuum than in air.

Concerning the surface state of the metal-semiconductor interface, one of the most significant properties is the Schottky barrier height formed at the interface. The correlation of it with the friction behavior was therefore examined. As indicated in table I, the barrier height depends on how the surface is prepared (chemically etched or cleaved) because the presence of surface films such as SiO_2 , for example, changes the surface state. Two types of prepared surfaces, chemically etched and cleaved, were available in this study. Friction coefficients in room air are plotted against the barrier height of a chemically etched surface (fig. 5). The sputter-cleaned surface is assumed to be similar to a cleaved surface in regard to barrier height. However, since the measurements of barrier height on a cleaved surface in vacuum were not completed for titanium and tantalum, the results for both chemically etched and cleaved

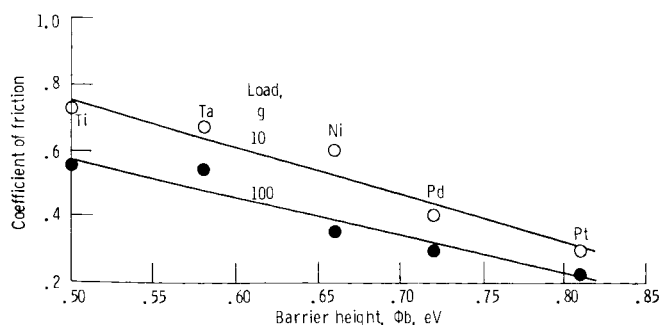


Figure 5.—Correlation between coefficient of friction in room air and barrier height of transition metals on chemically etched silicon surface. Sliding velocity, 1.4 mm/s.

surfaces of nickel, palladium, and platinum are presented (fig. 6).

Figure 5 indicates the coefficient of friction in room air as a function of barrier height for five metals on a chemically etched silicon surface at loads of 10 and 100 g. From titanium (barrier height $\phi_b = 0.50$ eV) to platinum ($\phi_b = 0.81$ eV), the coefficient of friction gradually decreased with increasing barrier height. The same relation between the coefficient of friction and the barrier height is presented in figure 6 for the metals in vacuum on both chemically etched and the cleaved silicon. For three metals, nickel, palladium, and platinum, there was a similar effect of barrier height on the coefficient of friction with two different surface preparations.

Figures 5 and 6 indicate that the coefficient of friction depended strongly on the Schottky barrier height formed at the metal-silicon interface. Metals with a higher barrier

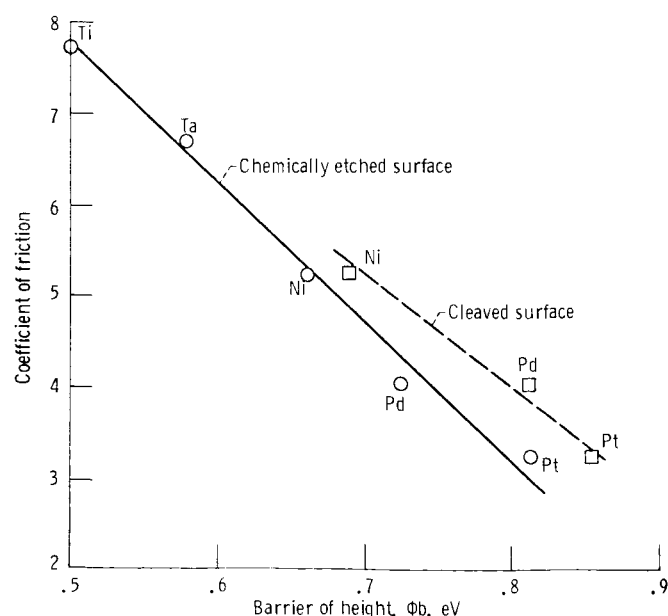


Figure 6.—Correlation between coefficient of friction in vacuum (10^{-9} torr) and barrier height of transition metals on chemically etched and cleaved silicon surface. Load, 10 g; sliding velocity, 0.2 mm/s.

height on silicon gave lower friction. There was a linear correlation between coefficient of friction and barrier height. Because of the presence of surface films formed before the experiments and chemisorbed films of gas molecules formed during sliding, the effect of the barrier height on friction appeared as a weaker relation in room air.

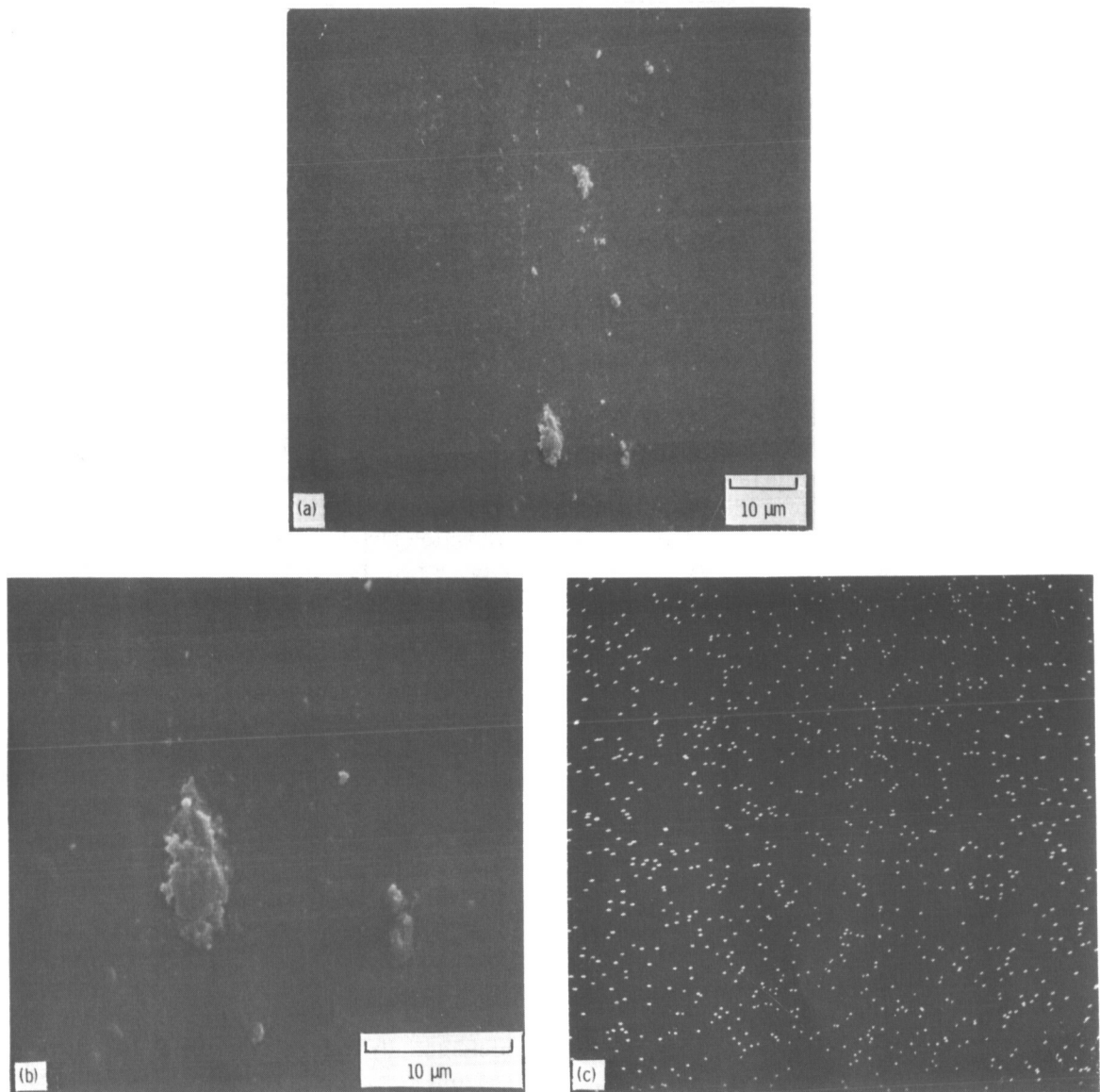
Although the barrier height is defined by the purely electronic properties of the metal-semiconductor interface, it dominates the tribological behavior of semiconductors in contact with metals. When a semiconductor comes into contact with a metal surface, the chemical activity between metal and semiconductor is strongly affected by the barrier height. The metal with a lower barrier height toward the semiconductor reacts more strongly and forms intimate bonding at the interface. This metal gives high friction in sliding contact with the semiconductor. Since the transition metals used in this experiment have very similar chemical characteristics toward silicon (i.e., high chemical reactivity with silicon and ability to form one or more compounds with silicon (refs. 19 to 21)), the experimental results exhibited a simple relation between barrier height and coefficient of friction for these five metals.

With nontransition metals, on the other hand, the coefficient of friction was generally lower than that for transition metals because of weak chemical affinity at the interface, as reported previously (ref. 8).

Figure 7 presents scanning electron micrographs of a wear track on a silicon surface which was in sliding contact with titanium in vacuum. Because of the strong bonding at the interface, many particles were removed from the surface and found on the wear track (fig. 7(a)). Figures 7(b) and (c) are enlarged micrographs of the particles and Ti-K α x-ray map by energy-dispersive x-ray analysis (EDXA). The debris was not metallic titanium but silicon particles which were fractured from the original silicon surface in the first stage and then subsequently back-transferred to the silicon surface. Back-transfer of silicon particles also occurred on all other tracks of silicon surfaces in sliding contact with metals. It is interesting that in metal-silicon contact particles were removed from the covalent silicon surface preferentially rather than from the metal surface in vacuum as well as in room air (refs. 7 and 8). This was a result of the brittle character of silicon.

Friction With Gallium Arsenide

The important correlation of coefficient of friction with Schottky barrier height was examined for another semiconductor, gallium arsenide, in contact with metals. The coefficients of friction for indium, nickel, copper, and silver sliding on the gallium arsenide (100) surface in room air are presented in figure 8. Motion was stick-slip only when the indium slid on gallium arsenide. The



(a) Wear track.
 (b) Particles on wear track.
 (c) Ti-K α map by EDXA of particles on wear track.

Figure 7.—Wear track of silicon (111) surface in sliding contact with titanium in vacuum (10^{-9} torr). Load, 10 g; sliding velocity, 0.2 mm/s.

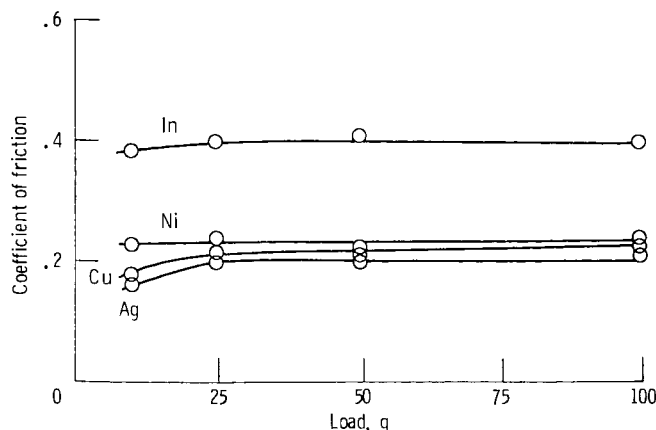


Figure 8.—Coefficient of friction as function of load for metals sliding on gallium arsenide (100) surface in room air. Sliding velocity, 1.4 mm/s.

coefficients of friction plotted in the figure are the maximum values measured in each sliding pass (the same plotting method as for the friction with silicon). The coefficient of friction for indium was the greatest among those of the four metals. With copper and silver friction was the lowest. The friction was even lower with all metals when a lower load was applied.

The coefficients of friction in vacuum (10^{-9} torr) are summarized in table III. Since motion was stick-slip with all metals in vacuum, the maximum peak values are presented in the table. The results in room air at a load of 10 g are also listed. The effect of particular metals in vacuum was similar to the results obtained in room air. The coefficient of friction for indium was the highest among those of the four metals. With copper and silver, the coefficients of friction were lowest, and there was little difference between them.

A correlation of friction behavior of gallium arsenide with Schottky barrier height was examined. Figure 9 presents the coefficient of friction in room air as a function of barrier height on chemically etched gallium arsenide surfaces at loads of 10 and 100 g. The same correlation between the barrier height and the coefficient of friction in vacuum is presented in figure 10. In figure

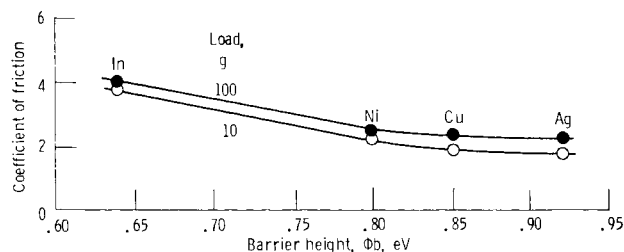


Figure 9.—Correlation between coefficient of friction in room air and barrier height of metals on chemically etched gallium arsenide surface. Sliding velocity, 1.4 mm/s.

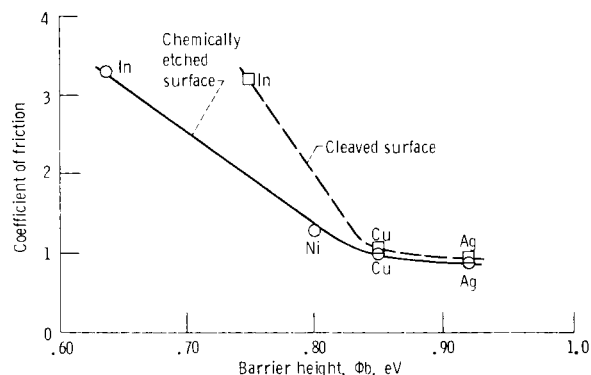


Figure 10.—Correlation between coefficient of friction in vacuum (10^{-9} torr) and barrier height of metals on chemically etched and cleaved gallium arsenide surface. Load, 10 g; sliding velocity, 0.2 mm/s.

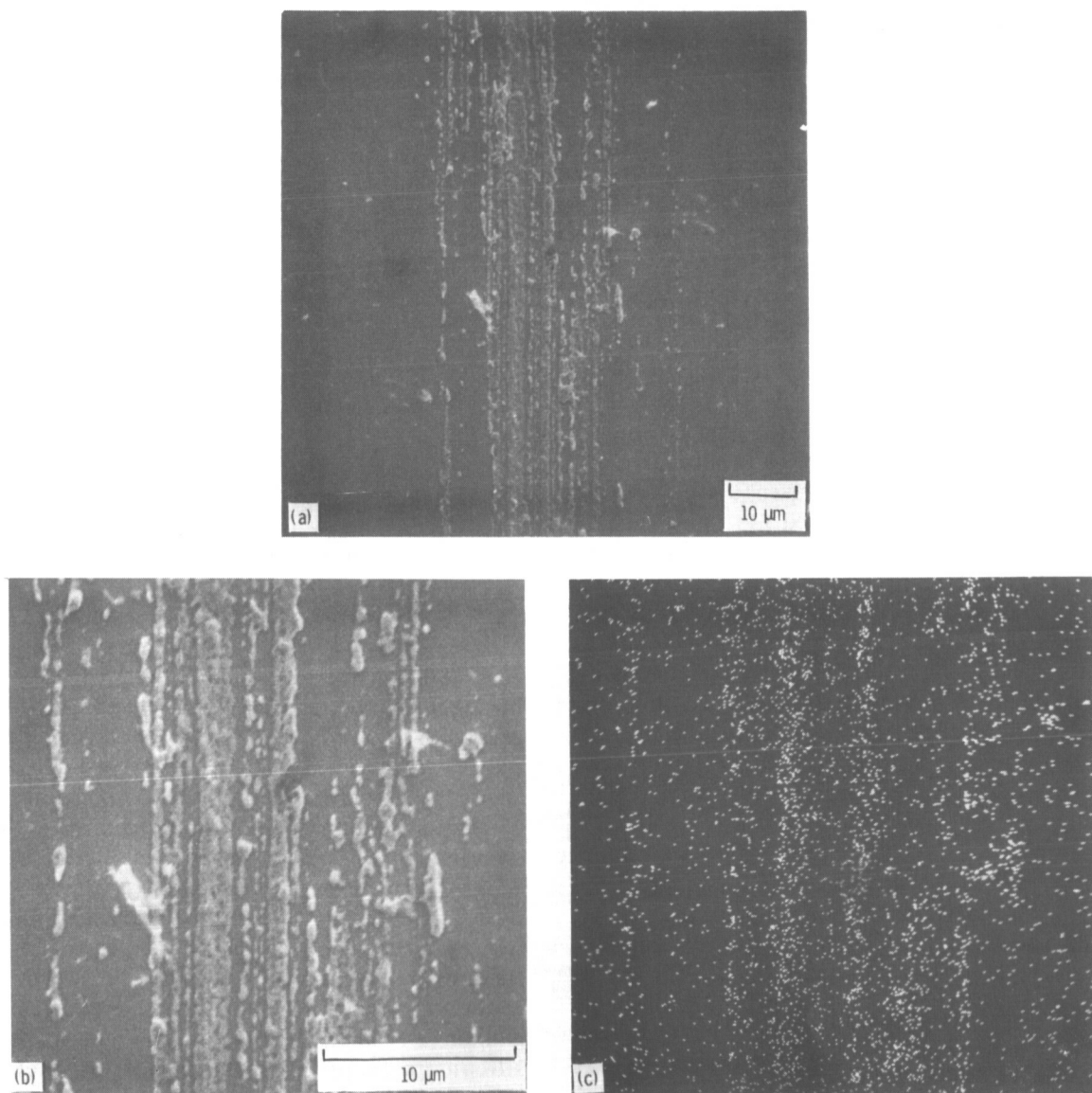
TABLE III.—COEFFICIENT OF FRICTION FOR METALS SLID ON GaAs IN VACUUM AND ROOM AIR

[Load, 10 g.]

Metal	Coefficient of friction	
	In vacuum (10^{-9} torr)	In room air
Indium	3.2	0.38
Nickel	1.3	.23
Copper	1.0	.18
Silver	.91	.17

10 the coefficient of friction is plotted against barrier height for both chemically etched and cleaved surfaces except for nickel. The influence of surface preparation on the correlation was not found. As exhibited in these figures, the coefficient of friction for gallium arsenide depended on barrier height. Indium, with the lowest barrier height, gave the highest coefficient of friction. Silver exhibited the lowest friction as a result of its very high barrier height. These effects appeared more clearly when the surface films were absent from the sputtered surfaces in vacuum. Since there is not a chemical characteristic common to the four metals in contact with gallium arsenide, the relation was not linear as with silicon in contact with transition metals. The experimental results, however, indicated that there was a close relation between barrier height and friction behavior for gallium arsenide.

Figure 11 shows a wear track on gallium arsenide in sliding contact with indium in vacuum. The surface of gallium arsenide was slightly different from that of silicon. On the wear track a large quantity of particles were found (fig. 11(a)). By the EDXA in figures 11(b) and (c), the particles were determined to be transfer particles from the indium surface. Because of the weak bonding at the interface, the particles were small, and surface fracture was minimal. This was also true with the other metals sliding on gallium arsenide.



(a) Wear track.
 (b) Particles on wear track.
 (c) In-K α map by EDXA of particles on wear track.

Figure 11.—Wear track of gallium arsenide (100) surface in sliding contact with indium in vacuum (10^{-9} torr). Load, 10 g; sliding velocity, 0.2 mm/s.

Summary of Results

Sliding friction behavior of the semiconductors silicon and gallium arsenide in contact with pure metals was studied. From the experiments in room air and in vacuum, the following were obtained:

1. The friction of semiconductors was sensitive to the contacting metals. With both silicon and gallium arsenide the friction behavior depended strongly on the height of the Schottky barrier formed at the metal-semiconductor interface. The metals with a lower barrier height gave a higher coefficient of friction as a result of strong bonding at the interface.

2. With silicon in contact with the transition metals, there was a linear correlation between the coefficient of friction and barrier height.

3. In room air the effect of barrier height was weak for both silicon and gallium arsenide. The presence of surface films masked the real character of the metal-semiconductor interface.

4. On the wear track of silicon in contact with titanium, silicon particles back-transferred. This was caused by the preferential removal of particles from the silicon surface as a result of the brittle character of silicon. In contrast to the silicon, on the gallium arsenide surface a large quantity of indium particles transferred to the surface, and surface damage was minimal. This was also true for gallium arsenide in sliding contact with other metals.

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Cleveland, Ohio, date

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16. Abstract Friction experiments were conducted for the semiconductors silicon and gallium arsenide in contact with pure metals. Polycrystalline titanium, tantalum, nickel, palladium, and platinum were made to contact a single-crystal silicon (111) surface. Indium, nickel, copper, and silver were made to contact a single-crystal gallium arsenide (100) surface. Sliding was conducted both in room air and in a vacuum of 10^{-9} torr. The friction of semiconductors in contact with metals depended on a Schottky barrier height formed at the metal-semiconductor interface. Metals with a higher barrier height on semiconductors gave lower friction. The effect of the barrier height on friction behavior for argon-sputtered cleaned surfaces in vacuum was more specific than that for the surfaces containing films in room air. With a silicon surface sliding on titanium, many silicon particles back-transferred. In contrast a large quantity of indium transferred to the gallium arsenide surface.					
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